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LIQUID-METAL BINARY CYCLES FOR STATIONARY POWER

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LIQUID-METAL BINARY CYCLES FOR STATIONARY POWER*

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SUMMARY

One of the major consumers of energy is the electric power generating industry, which uses over 25 percent of the total energy consumed in this country and is expected to double its output in the next 10 years. This predicted growth may be restricted due to limited world and domestic fuel supplies. One way of increasing power generating capabilities within currently available fuel supplies is to increase plant efficiencies. Large, modern, fossil-fueled steam powerplants attain efficiencies of about 40 percent, and the average nuclear powerplant efficiency is about 33 percent. It is proposed that significant increases in plant efficiencies can be attained by the use of "topping" cycles that employ liquid-metal Rankine cycles at elevated temperatures in conjunction with conventional steam cycles at lower temperatures. The mercury topping cycle was used successfully from 1920 to 1950 by some utilities but was displaced by improved steam-cycle power generating plants. Considerable government effort during the 1960's has introduced advanced technologies in the mercury and alkali-metal Rankine-cycle systems which could be available for consideration as "topping" cycles. An overview of this technology, possible system applications, the required development, and possible problem areas are discussed herein.

INTRODUCTION

It is predicted that the electric power generating capacity of the nation will grow substantially in the next three decades. The projected growth has been estimated as increasing from a generating capacity of 3×10^5 megawatts in 1970 to 1.5×10^6 megawatts in the year 2000. This anticipated growth is required to produce an increase of goods and services to an expanding population and must be accomplished in spite of an increased world energy demand and decreasing fuel reserves. The United States, for example, is faced with a rather imminent depletion of natural gas and oil supplies but, fortunately,

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has an appreciable fossil fuel reserve in the forms of coal and oil shale which will require significant development before becoming economical to mine and refine.

Environmental problems associated with the production, processing, and consumption of energy are other considerations. The possible contamination and depletion of water sources due to mining and processing operations, atmospheric contamination by sulphur dioxide and particulate matter from fossil fuels, thermal pollution of waterways, and the escape of radionuclides from nuclear powerplants and fuel reprocessing plants are all related to electric power production. The energy shortage and environmental factors, material and equipment availability, and the escalating costs of money, material, and labor are all inhibiting the growth of electric power production.

The electric power industry today accounts for approximately one-fourth of the total energy consumption in the United States. By 1985 the industry is expected to consume about one-third of the energy produced. Consequently, methods to economically minimize fuel consumption and environmental problems will have to be developed shortly if this nation is to maintain a plentiful supply of electrical energy.

Approximately 80 percent of the electricity generated in the United States is produced by steam powerplants heated by the combustion of fossil fuels. Nuclear systems account for another few percent, and their number is increasing rapidly. The average conversion efficiency of all steam powerplants in the country is only about 33 percent. Thus, about two units of waste heat must be released to the environment for every one unit of electricity produced. Increasing the conversion efficiency would therefore reduce the amount of waste heat produced, and, in addition, reduce both the consumption of fuels and emissions of combustion products to the atmosphere.

The efficiency of steam powerplants has increased from less than 20 percent in 1920 to about 40 percent for today's most modern fossil-fueled plant. This increase has been brought about mainly by the higher steam turbine-inlet temperatures and pressures, in turn, made possible by advances in materials technology. In the future, however, large increases in steam powerplant efficiencies are not expected to materialize. The performance improvements resulting from substantially higher temperatures and pressures are believed to be too small to warrant the added costs, and some technical questions exist as to the feasibility of raising steam powerplant operating conditions. In addition, the development of compatible high-strength materials for fluid containment and rotating hardware would substantially increase capitalization costs.

Liquid-metal (mercury) Rankine power systems have been used in the past by utilities to improve powerplant efficiencies. These mercury powerplants were used as "topping" units; that is, the waste heat of the liquid-metal cycle was transferred to a lower-temperature, conventional steam plant to generate additional electricity. One such station, the Schiller plant, constructed in 1950, converted heat to electricity with an efficiency that exceeded, for its size, any other powerplant in the world (ref. 1).

The development of the topping cycle for stationary power use ended, for technical and economic reasons, with the construction of the Schiller station. However, during the 1960's, several advanced power conversion concepts were pursued as possible providers of electric energy in space. Among these were mercury and potassium Rankine cycles. Relatively small mercury conversion systems and components were endurance tested at temperatures to 675°C (1250°F). Likewise, potassium components, including turbines, were operated at temperatures of 815°C (1500°F) and above. The results of these efforts have demonstrated the technical feasibility of liquid-metal Rankine power conversion systems operating at high temperature and, moreover, suggest their use for topping plants for improved-efficiency stationary powerplants on Earth. The following sections review the status of the technologies of mercury and potassium cycles and their potential applications.

Modern steam powerplants have relatively high conversion efficiencies (up to 40 percent) and have generating capacities of up to about 1000 megawatts. Utilities try to operate such plants continuously and at full capacity as much as possible to minimize generating costs. Typically, these plants are used to satisfy that portion of the electric power demand that does not vary very much; that is, they constitute the baseload capacity of a utility's power generation system.

Liquid-metal binary cycles share similar characteristics with steam Rankine powerplants. They have the potential of high conversion efficiency, they will likely produce lower-cost power in plants of large capacity rather than small, and they will operate more efficiently at design capacity rather than at partial load. Consequently, liquid-metal topping cycles would likely find application primarily as base-load plants.

Mercury topping cycles, because of the physical and thermodynamic properties of the mercury working fluid, require a heat source that operates in the temperature range of about 535°C to 700°C (1000°F to 1300°F). Light-water reactors are limited to temperatures well below this range. The liquid-metal fast-breeder reactor (LMFBR) now being developed by the Energy Research and Development Administration is expected ultimately to operate with a coolant outlet temperature of 600°C to 650°C (1100°F to 1200°F). A mercury-steam binary or topping plant, therefore, appears adaptable for use with LMFBR. The high-temperature, gas-cooled reactor (HTGR) has coolant outlet temperatures above 700°C (1300°F) and could probably be used with mercury binary cycles as well.

The potassium Rankine cycle is potentially useful at temperatures above 760°C (1400°F). At present, with the possible exception of the HTGR, heat sources for the potassium cycle are nonexistent and use of the potassium topping cycle with HTGR has not been suggested. However, two organizations, the General Electric Company and the Oak Ridge National Laboratory, have proposed the use of potassium-steam binary cycles with fossil-fueled heat sources for large, baseload plants. Both groups acknowledge the

need to develop high-temperature potassium furnace boilers as part of a program to bring potassium topping cycles to fruition.

A significant fraction of the fossil-fueled steam powerplants in the United States are relatively small, inefficient units that may become uneconomical to operate over the next few decades. In some cases, the turbomachinery of these plants will still have useful life, but the boiler may need replacement. The potassium topping cycle may serve as a means of upgrading the performances and, therefore, the economies of these small plants.

HISTORICAL BACKGROUND

Mercury Topping Cycles

Between 1922 and 1950, several fossil-fueled mercury topping cycles were constructed for utility and industrial use by the General Electric Company. A brief discussion of the plants, based primarily on references 1 to 12, is presented in this section. Table I (adapted from ref. 6) lists the performance data of these plants.

The mercury binary plants listed in table I were used to generate electricity and in certain installations process steam. The plants were by today's standards, very small - the largest had a capacity of 47 megawatts (20 MW from Hg topping). Typical conditions at the inlet to the mercury turbine were 510°C (950°F) and a pressure of about 90 newtons per square centimeter (130 psia). The Schiller plant, one of the last mercury topping cycles to be built, had an efficiency of slightly over 37 percent (which is commonly expressed as a net heat rate of about 9200 Btu/kW-hr).

These mercury plants demonstrated their durability: the original South Meadow Station of the Hartford Electric Light Company operated from 1928 until 1947 when it was dismantled. During this interval, it accumulated more than 119 000 service hours, roughly 70 percent of the total life of the plant. Kearny, placed into service in 1933, achieved in excess of 86 000 service hours by 1950 and continued in operation past the 110 000-hour mark.

The reliability of the mercury turbines was excellent. For example, when the original turbine in the South Meadow plant was dismantled, it was the first time in 16 years that it had been opened. Examination of the turbine internals showed no failures and only minor erosion of the blades and other parts of the turbine. Kearny's turbine and the two mercury turbines of the Schiller plant each achieved total operating times in excess of 110 000 hours.

The mercury topping cycles were not without development problems. Primarily, these were related to the operation of the boiler. The first mercury boilers were char-

acterized by unpredictable performance and tube plugging and failure. Mercury boiling heat-transfer coefficients varied as much as an order of magnitude over the course of a few days, and some boilers would achieve design performance only after months of operation. This behavior was attributed to variable wetting of the tube inner surface by the mercury. The plugging problem was found to be the result of mercury corrosion of the tube material, typically, low carbon steel. Solutions to some of these difficulties were obtained by the General Electric Company.

A new boiler material, Sicromo 5S (5 chromium, 0.5 molybdenum, 1.5 silicon) was more resistant to mercury corrosion than the previously employed material and had the advantage of superior strength at high temperatures. Although Sicromo 5S was used in the mercury boilers of later plants, the corrosion effects of boiling mercury were not eliminated. An extensive corrosion test program at GE resulted in the identification of additives to the mercury, principally magnesium and titanium, that effectively eliminated the corrosion problem. The additives inhibited the corrosion process and caused the mercury to wet the boiler tube surfaces, thus significantly improving the heat-transfer performance of this component. These discoveries made possible the use of simple flow circuits in the boiler design and a single-drum boiler unit that reduced the required mercury inventory by permitting vapor to occupy the tubes above the drum level. The only pressure parts that contained mercury at startup were those portions of the furnace tubes below the drum and the downcomer supply pipes and lower headers. The quantity of mercury required was thus only a fraction of that which would be necessary if the boiler drum were mounted in the usual position at the top of the furnace and if all of the tubes were filled with liquid (ref. 6). To prevent excessive consumption of additives, methods were developed to minimize air and water seepage into the mercury system. This involved redesigning the mercury turbine seal, sealing the stems of valves, and leak checking the mercury condenser-steam generator as well as all welds and flanges. At the Kearny plant, air seepage was reduced by these techniques from 8.5 to less than 0.011 cubic meter per hour (300 to less than 0.4 cubic feet per hour).

Mercury topping cycles were not built after 1950. Improvements in steam power-plant operating conditions resulted in efficiencies that exceeded those of the mercury plants. Moreover, steam plant capacities grew substantially larger than the mercury plants, resulting in further economies. Finally, the price of mercury fluctuated sufficiently as to render the construction of new mercury topping cycles uncertain and risky.

During the 1960's, the technology for mercury Rankine cycles was actively pursued. The Systems for Nuclear Auxiliary Power (SNAP) program, for example, developed a 35- to 90-kilowatt mercury system (including nuclear heat source) for use in space missions. This work was conducted at turbine-inlet temperatures of 650° to 700° C (1200° to 1300° F). A review of the advances made in mercury technology provided by the space power program is presented in a later section.

Potassium Topping Cycles

There is no history of use of potassium topping cycles in utility powerplants.

During the 1960's, potassium Rankine research and technology efforts were conducted under the sponsorship of the National Aeronautics and Space Administration, the Atomic Energy Commission, and the Air Force. This work was aimed at developing a powerplant of 300 kilowatts to several megawatts capacity for use in space.

Studies have been conducted of potassium topping cycles for central station power in the early 1960's. More recently, A. Fraas of ORNL proposed such a topping cycle with the molten-salt reactor (ref. 13). Fraas also suggested a gas-turbine - potassium - Rankine - steam-Rankine ternary system utilizing the heat of combustion of clean liquid or gaseous fuels (ref. 14) or solid coal in a fluidized bed (ref. 15). The General Electric Company has described a more-conventional-design potassium topping cycle that burns coal (ref. 16).

SYSTEM CHARACTERISTICS

General

In its simplest form, a Rankine cycle converts heat to work (mechanical energy) by a process that involves boiling a working fluid, expanding the vapor through a turbine, condensing the turbine exhaust vapor, and pressurizing and recirculating the fluid to the boiler by means of a pump. The steps of this process are shown schematically in the temperature-entropy diagram of figure 1. The Rankine cycle closely approximates the ideal or Carnot cycle because most of the heat is added or rejected at constant temperatures. Practical steam Rankine powerplants utilize more complex cycles than shown in the figure that increase plant efficiency or extend component life. Nevertheless, the cycle shown in the diagram illustrates the main processes of a steam powerplant.

Figure 2 is a simplified temperature-entropy diagram for a liquid-metal Rankine binary cycle. The lower cycle corresponds to the steam system shown in the previous diagram. The upper, higher-temperature cycle is composed of processes identical to the steam cycle, boiling, expansion through a turbine, etc. However, the heat released by the condensation of the turbine exhaust vapor is used to generate steam for a conventional steam turbine, rather than being rejected to the surroundings. The efficiency of the binary cycle is superior to the steam system alone because thermal energy can be utilized at a higher cycle temperature. The full gain in efficiency, corresponding to the maximum temperature, cannot be realized, however, because of losses associated with the transfer of heat from the condensing metal vapor to the steam across a finite temperature difference.

The peak temperature of a binary cycle is, in theory, limited only by the temperature of operation of the containment material. In practical systems the maximum temperature will be determined by a trade-off between the costs of the powerplant equipment and the gain in conversion efficiency. Both the plant's performance and its costs are strongly influenced, in turn, by the physical and thermodynamic properties of the liquid-metal working fluid and its compatibility with containment materials. Materials compatibility, a broad field, will be discussed briefly in subsequent sections. A description of the properties of liquid metals as they pertain to conversion systems is outlined below.

Ideally, a working fluid for a high-temperature Rankine cycle should possess the following characteristics: The fluid should be chemically stable, unreactive, and readily purified to minimize the deleterious effects of contaminants. The critical temperature and pressure should be higher than the cycle heat addition temperature to insure constant temperature heat addition. High heats of vaporization are likewise desirable to minimize flow rates and, therefore, pumping power requirements. High vapor densities (low specific volumes) are beneficial in reducing the size of the turbomachinery and other components. Other desirable properties include: high thermal conductivity, high sonic velocity in the vapor, low specific heat of the liquid, and a low melting point.

Table II compares the properties of mercury, potassium, and water (because water is so widely used as a working fluid). Figure 3 is a plot of the vapor pressure of these fluids as a function of temperature. From these and other data certain generalizations about mercury and potassium may be made.

The latent heat of vaporization of mercury is roughly one-tenth that of water. This implies relatively high flow rates and pumping penalties. The vapor pressure at 700°C (1300°F) is about 524 newtons per square centimeter (760 psia). Above 700°C (1300°F) the vapor pressure of mercury increases rapidly. At about 200°C (400°F) the vapor pressure falls to about 0.28 newton per square centimeter (0.4 psia), and the vapor specific volume at this condition is nearly 7.36 cubic meters per kilogram ($118\text{ ft}^3/\text{lbm}$). This represents about the lower limit on practical mercury condensing temperatures (ref. 17). Mercury, because of its high molecular weight, exhibits a low sonic velocity. This property imposes low turbine tip speeds that might result in the need for multiple-flow turbines. On the other hand, a high molecular weight suggests fewer turbine stages, which is a cost advantage. Finally, mercury tends not to wet metal surfaces (except that above 535°C (1000°F) it fully wets tantalum). This tendency for non-wetting and the high surface tension of liquid mercury causes this fluid to form into tiny spheres or droplets. As a result, fog flow, the two-phase flow of a mixture of mercury droplets and vapor, is frequently encountered in boilers and results in generally poor heat-transfer performance.

Surprisingly, the properties of potassium compare favorably with water. But the vapor pressure of potassium is relatively low: at 760°C (1400°F) it is 10 newtons per square centimeter (15 psia), and at 980°C (1800°F) it is 56 newtons per square centi-

meter (81.2 psia). Consequently, over this temperature range, the wall thicknesses of potassium boiler tubes will likely be determined by consideration of stresses other than those arising from internal pressure. At 535°C (1000°F) the vapor pressure of potassium is about 0.76 newtons per square centimeter (1.1 psia), and the vapor specific volume is about 21.9 cubic meters per kilogram ($350\text{ ft}^3/\text{lbm}$). Both values suggest that a potassium condensing temperature substantially lower than 535°C (1000°F) may be impractical because of the possible need for large, multiple flow turbines and large turbine exhaust flow areas. Liquid potassium wets almost every conventional alloy surface at temperature levels of interest. Potassium has a relatively high melting point (63.2°C ; 145.8°F), which imposes concerns for freeze-up in a powerplant. It is also readily oxidized; hence, contact with air and water must be avoided.

Cesium, another alkali metal, has also been proposed as a working fluid for binary cycles. The properties of this fluid are also shown in table II. The advantage of cesium over potassium is that cesium has a higher molecular weight and would require fewer turbine stages.

Mercury

The mercury binary cycle is a conversion system that could eventually be used with the liquid-metal fast breeder reactor (LMFBR). The initial reactor output operating temperature for the LMFBR is expected to approach 535°C (1000°F). Subsequent development is expected to raise reactor outlet temperatures to the 650°C (1200°F) level or possibly higher. The use of a mercury topping cycle at this outlet temperature would result in a significant increase in plant efficiency over that of a conventional steam cycle.

Figure 4 presents a schematic diagram of an LMFBR-steam powerplant of 1000 electrical megawatts nominal capacity operating at a reactor outlet temperature of 620°C (1150°F) (ref. 18). The net efficiency of this plant is reported to be 41.6 percent. For comparison figure 5 is a schematic of an LMFBR-mercury-steam binary plant having a reactor outlet temperature of 650°C (1200°F), a temperature that might eventually be reached by the LMFBR, and employing a once-through mercury boiler. The cycle configuration and reactor thermal power level shown in this figure were selected to utilize the same steam powerplant shown previously. As indicated, an extra 200 electrical megawatts can be generated by the introduction of the mercury cycle - but, at the expense of more equipment and increased system complexity. The mercury binary cycle of figure 5 would convert heat to electricity at a plant net efficiency estimated to be about 46 percent (private communication with G. Barna of Lewis). Coupling the LMFBR to the mercury conversion loop only, that is, eliminating the sodium-to-steam heat exchangers, results in a higher net efficiency and reduces the possibility of a sodium-water reaction. These predictions are preliminary and indicate only the level of improvement that can be

achieved. More extensive analyses would be required to fully define the performance of a mercury binary cycle with the LMFBR.

If the mercury system were developed for use with LMFBR, its adaptation to fossil heat would be given strong consideration. One interesting concept for such a plant is to use a combustion furnace that heats liquid NaK (private communication with R. E. English of Lewis). In turn, NaK delivers heat to the mercury working fluid, as with the nuclear heat source. The advantages of this concept are that the design of the furnace is simplified and that the NaK to mercury boiler developed for the LMFBR system could be used in the fossil-fueled plant. The results would be reduced risks and development time and costs. The economic feasibility of this concept for mercury topping cycles for fossil fuels has not been evaluated.

Potassium

A potassium binary cycle, like steam systems, should be capable of burning the fossil fuels such as coal, oil, and natural gas. With the introduction of coal gasification and liquefaction in this country, the clean fuels derived from these processes will represent convenient forms of energy. Other forms of energy, such as char, a byproduct of the coal to gas conversion process, or even municipal wastes, which have been used by at least one electric power utility, are also possible fuels.

Figure 6 (from ref. 16) presents potassium binary cycle efficiencies as a function of turbine inlet temperature for three condensing temperatures. These curves are applicable to a fossil-fueled plant and therefore include a boiler efficiency of 0.90. Cycle efficiencies of 50 to 55 percent or more over the range of turbine-inlet temperatures between 760°C and 980°C (1400°F and 1800°F) are suggested by this figure. The computations for this graph assumed that all the energy entering the steam portion of the binary cycle was derived from the condensing potassium. This implies the availability of high-temperature air preheaters in the potassium furnace, for without such preheaters some of the combustion energy would likely have to be added directly to the steam. This would reduce the cycle performance from that shown in figure 6. Efficiencies of about 46 percent can, therefore, be expected with first-generation potassium topping cycles operating at a 760°C (1400°F) turbine-inlet temperature. A schematic for such a plant is given in figure 7 (from ref. 16).

Reference 14 presented a conceptual design of a ternary system - a gas-turbine - potassium-Rankine - steam-Rankine powerplant that burns a clean liquid or gaseous fuel. A schematic of this system is shown in figure 8. The gas turbine drives both a compressor that pressurizes the combustion side of a furnace and a separate generator. The furnace serves as the combustor for the turbine and as the heat source for the potassium

boiler. The gas turbine operates at an inlet temperature of about 925°C (1700°F), the potassium turbine at 835°C (1540°F), and steam at 565°C (1050°F). The resultant powerplant efficiency predicted by reference 14 is about 53 percent.

There is no information available concerning weight or volume per unit output of either the mercury or potassium topping cycle. In general, both are relatively low-pressure systems. As such, the vapor portions of these systems will tend to be larger in flow cross sectional area than the corresponding equipment in steam powerplants. By a similar argument, the containment wall thicknesses may be thinner because of the lower pressure stress levels. A specific powerplant design is required to quantify these characteristics.

STATE OF THE ART

Mercury

The most recent effort directed toward the development of a mercury Rankine system since the topping cycle work described under HISTORICAL BACKGROUND was NASA's SNAP-8 Power Conversion System. The objective of this work was to demonstrate a reactor-heated, mercury conversion system of 35 to 90 electrical kilowatts capacity and of high reliability and long life for use by man in space. An outline of the status of this work is presented in this section. Reference 19 describes the status of the SNAP-8 system in detail.

Turbine. - Under the SNAP-8 program, a four-stage, axial-flow turbine (fig. 9) was built and tested as part of the operation of a complete mercury system. The sections of the turbine exposed to mercury were fabricated of a cobalt-chromium-nickel alloy, S-816. The first two stages were partial admission, the last two were full admission. Bearings for this machine were oil-lubricated. The combination of a viscopump, a slinger pump, and a molecular pump, connected in series, constituted the seal (fig. 10) for the mercury turbine. This seal arrangement operated by holding a mercury liquid-vapor interface at a precise location and limiting the flow of escaping vapor to a vacuum vent at a controlled rate of about 4.5 kilograms (10 lb) per 10 000 hours. The turbine was designed to operate at a 56 percent efficiency and to produce about 60 kilowatts (80 hp) at an inlet temperature of 675°C (1250°F) and an inlet pressure of 17.2×10^5 newtons per square meter (250 psia). After the turbine was operated for about 8700 hours it was disassembled and examined. The results of this examination indicated that all mechanical components were in good condition. Moisture erosion of the turbine blades was negligible. The life expectancy of the turbine based on these findings was estimated to exceed the desired 5 years. The turbine was reassembled and run a total of 10 823 hours before the testing of this component was ended.

Boiler. - The SNAP-8 boiler development was aimed at providing dry superheated mercury vapor at about 675°C (1250°F) and 172 newtons per square centimeter (250 psia) at the boiler exit. (The corresponding saturation temperature at 172 N/cm^2 (250 psia) was 565°C (1050°F).) The heating fluid was sodium-potassium (NaK) eutectic, and the thermal duty was 600 kilowatts: the NaK peak temperature was 700°C (1300°F), or 100°F above the LMFBR goal. Initial SNAP-8 boilers were fabricated of Haynes 25, Sicromo 9M, and Sicromo 9M-modified. Operation of these units at the nominal conditions cited resulted in severe corrosion and variable thermal performance due to the unpredictable tube wall wetting by the mercury. (Additives such as magnesium and titanium were considered impractical for use in the once-through space boiler.) Tantalum was found to be fully compatible with boiling mercury at the SNAP-8 temperature levels, and laboratory tests indicated it was completely wetted by this fluid above 535°C (1000°F). Because of these characteristics, tantalum was selected as the material to contain the boiling mercury. Four mercury boilers utilizing tantalum tubes were designed and fabricated. The mercury flowed inside seven tantalum tubes, each of which was enclosed in a stainless-steel tube. The annular space between the tubes was filled with stagnant NaK, an excellent heat-transfer medium. The heating fluid, flowing NaK, passed around the outside of the stainless-steel tubes in a direction counter to the mercury flow. This double-containment design, illustrated schematically in figure 11, provided additional protection from leaks and eliminated the possible contamination of the tantalum from oxides or other impurities in the flowing NaK. The four boilers were tested for a total of 25 000 hours, one of which was operated for over 15 000 hours. The thermal and hydraulic performance of these heat exchangers was extensively mapped over a wide range of conditions. The post-test examination of the boilers gave the following results. The tantalum remained free of corrosive attack from the boiling mercury, confirming one of the reasons for its selection. In the chemically clean, oxygen-free state, the tantalum was wetted by mercury and therefore gave stable, predictable boiler performance. But the introduction of contaminants such as lubricating oil or oxygen offset the high heat-transfer rates of boiling mercury by as much as an order of magnitude or more, due to the occurrence of nonwetting. The lubricating oil, in addition, formed a carbonaceous deposit on the tantalum that imparted a minor thermal resistance. The effects of these contaminants were, in the small quantities encountered during testing, reversible: oxygen in the tantalum diffused into the static NaK surrounding the tube, and the carbonaceous deposit was partially removed by the flowing mercury. The complete SNAP-8 system (shaft seal and all) was operated in air for over 7000 hours with only a slight drop in system performance.

Other components. - Mercury pumps, valves, and condensers were built and performance tested under the SNAP-8 program. These components were also subjected to component and system endurance testing. At least one unit of each of these components achieved 10 000 hours of operation without degradation.

Materials. - The findings of a study to determine the compatibility of materials with high-temperature mercury are summarized as follows: Conventional chromium-molybdenum steels, the stainless steels, Haynes 25 (L-605), etc., may be safely exposed to liquid mercury at temperatures below 370°C (700°F) and with minimal corrosion below about 480°C (900°F). These alloys may be used to contain mercury vapor at 650°C (1200°F) or more, providing the moisture content of the vapor does not exceed 50 percent. In the boiler, however, the mercury undergoes large and rapid changes in vapor quality and usually achieves high fluid velocities. Under these difficult conditions the alloys just cited are unsuitable for use. Tantalum and niobium are suitable mercury containment materials for use in the boiler above 480°C (900°F). Tantalum was demonstrated to be compatible with mercury to 675°C (1250°F).

In summary, a firm base of technology exists for using mercury Rankine systems in combination with either the LMFBR or HTGR and possibly with fossil fuels and a NaK primary loop. Experience with mercury powerplants in both central power stations and in the space program defines a path for successful use of such systems; however, additional study is required to define the capital costs of mercury systems.

Potassium

During the 1960's, various government agencies were engaged in the development of potassium (and cesium) Rankine space power systems. Table III (adapted from ref. 20) summarizes the experience accumulated with alkali metal components and systems in this country. A brief discussion of the highlights of this work is given in this section; more extensive summaries are available in references 21 and 22.

Turbines. - Several potassium turbines were fabricated and tested. The largest of these were two- and three-stage units that employed oil-lubricated bearings and had capacities of 185 and 250 kilowatts (250 and 335 hp), respectively. The measured efficiencies of these turbines were about 75 percent, confirming design predictions. The blades and disks were, for the most part, fabricated of nickel-based alloys. Each turbine was tested for 5000 hours at an inlet temperature of about 815°C (1500°F) to determine moisture (liquid) erosion effects (see fig. 12). The two-stage turbine, on completion of its endurance run, exhibited negligible erosion. The three-stage turbine, operating at somewhat higher moisture levels, showed microscopic evidence of erosion at the tips of the third-stage blades. The three-stage turbine was subsequently rebuilt incorporating rotor and stator moisture-removal devices and, at the turbine exhaust, a vortex moisture separator. The designs of the rotor device and the vortex separator were based on steam-turbine practice. The effectiveness of the removal of the turbine condensate by these devices was measured with potassium vapor entering the turbine at 815°C (1500°F). The effectiveness of the rotor and vortex devices compared reasonably well

with those obtained for similar devices in steam turbines. In general, no limiting problems were encountered during the course of the testing of the potassium turbines.

Boilers. - Several potassium boilers have been tested for thousands of hours over the temperature range of 760° to 1200° C (1400° to 2200° F). This work has resulted in correlations of the heat-transfer coefficients and pressure losses for the major boiling potassium regimes. Computer programs for the thermal and hydraulic design of potassium boilers, based on these correlations, have been formulated and applied. In general, however, the boiler work has been conducted with relatively small equipment, typically less than about 150 thermal kilowatts, in which contamination by oxygen and other impurities could be strictly limited. The largest potassium boiler ever built was a stainless steel, natural gas-fired, recirculating unit with an output capacity of 3 thermal megawatts. This boiler supplied potassium vapor at 815° to 870° C (1500° to 1600° F) for more than 10 000 hours for the testing of the two potassium turbines already described. Some difficulties were encountered with the boiler during the 10 000-hour period due, at least in part, to the low strength of the stainless steel at the temperatures of operation.

Condensers. - Relatively small potassium condensers have been tested at temperatures between 600° to 870° C (1100° and 1600° F). Thousands of hours of operation have been accumulated. As with the boilers, heat-transfer data have been correlated and incorporated into computer programs for designing condensers.

Other components. - Electromagnetic and mechanical pumps have been built and successfully endurance tested (refs. 23 and 24). Throttle and shut-off valves have likewise been tested. The largest of these, an 8-inch valve, was used to regulate the flow of potassium vapor at about 870° C (1600° F) for more than 10 000 hours.

In summary, a firm base of technology for potassium Rankine systems exists, albeit at component sizes well below that required for stationary powerplants. Additional study is required to define the costs of system assembly and of system repair following unplanned shutdowns.

REQUIRED DEVELOPMENT

Mercury

The technology of high-temperature mercury topping cycles for the liquid-metal, fast-breeder reactor presently requires the use of tantalum or an equivalent refractory metal for lining the tubes of the boiler. Bimetallic tubing size and length are presently limited by available fabrication equipment. To obtain the sizes and lengths of bimetallic tubing required for a commercial powerplant, the existing fabrication equipment will have to be upgraded or techniques to make reliable bimetallic tube-to-tube joints will

have to be developed. In addition, other joining techniques, involving the tantalum liner and the tube headers, may have to be evolved and proven. Suitability of the cheaper niobium requires confirmation by test of a boiler.

The shaft seal of the mercury turbine must limit the introduction of oxygen and other contaminants (such as oil) into the conversion loop in order to sustain mercury-wetting of the boiler tubes and to prevent oxidation of the tantalum. Technology from the commercial powerplants and from the SNAP-8 space-power program should be used for design and test of a full-size shaft seal.

SNAP-8 boilers incorporated the use of long, small-diameter mercury flow passages at the inlet (ref. 25). Their use was based in part on the nonwetting behavior of mercury encountered in the early phases of the program. An alternative boiler design, based on mercury acting as a wetting fluid and not involving small-diameter passages, was tested and proven equally satisfactory (ref. 26). Thus, two boiler designs have both been demonstrated. The selection of one of these designs and the construction and test of a portion or module of the full-scale boiler is needed.

The development of the mercury-condenser - steam generator also requires the testing of a module of the full-scale unit. Although water will not react with mercury, it can cause the oxidation of tantalum. As such, a highly reliable steam generator must be built and then instrumented to rapidly detect leaks in this unit.

The successful completion of this development work would set the stage for the construction of a mercury binary cycle of pilot plant scale.

Potassium

Scale-up of the key components of the potassium cycle is necessarily required before construction of even a pilot plant can be considered. A full-scale module of both the potassium boiler and the potassium-condenser - steam generator would have to be performance tested and operated for a length of time to insure confidence in the design and materials of construction. A similar requirement exists for the test of a full-scale turbine shaft seal (fig. 13). In parallel with this, improvements in the methods of fabricating certain alloys into disks and blades in the sizes required by the potassium turbine will also be necessary. The long-term compatibility of potassium-containment materials with combustion products may likewise have to be assessed, depending on the selection of fuel and combustion technique. On completion of these developments, the construction of a pilot plant and, eventually, a demonstration plant would be necessary.

The Oak Ridge National Laboratory, under a grant from the National Science Foundation, has begun the construction of a module of the potassium boiler proposed for the topping cycle of reference 14. This boiler has an output capacity of several megawatts and is designed to operate at 845°C (1550°F).

PROBLEM AREAS

Mercury

The mercury binary cycle is faced with several problems, both technical and economic, which are discussed in the following paragraphs.

At present, only the refractory metals, tantalum and niobium - 1-percent zirconium (Nb-1Zr), can be used to satisfactorily contain boiling mercury at temperatures above 535°C (1000°F) (ref. 19). Of these, the unalloyed tantalum is the containment material of choice; Nb-1Zr has the potential for forming low-melting point eutectics when contaminated with base metals. Tantalum is fully wetted by mercury above about 535°C (1000°F). However, it must be protected from oxidation and is very expensive. The use of tantalum may, therefore, be restricted to a thin liner to protect the pressure-containing tubes from corrosive attack. The metallurgical bonding of 0.051-centimeter (0.020-inch) thick tantalum tubes to the inside of 6-meter (20-foot) long, small diameter (1.9 cm; 0.75 in.) stainless-steel tubes has been achieved on a developmental basis only. The capability to bond still thinner layers of tantalum to larger diameter, longer tubes and still preserve the corrosion protection essential to mercury boilers does not exist at present. The impact of the cost of tantalum on the economics of a mercury binary plant is unknown and requires evaluation.

Mercury is an expensive fluid, and its price has been, historically, very unstable. In 1965, for example, mercury sold (ref. 27) for more than \$20 per kilogram (\$9/lb), and in 1971 for about \$7.80 per kilogram (\$3.50/lb). World yearly consumption of this metal reached a peak of 300 000 flasks (34.5 kg or 76 lb per flask) in the mid 1960's and has since dropped about 6 percent to 280 000 flasks. Because of mercury's cost, limited production, and high density (about $13\,500\text{ kg/m}^3$; 840 lb/ft^3), the design of the components of the mercury conversion system must aim at minimizing the mercury inventory. The recirculating boiler, used in the mercury topping plants built by GE in the past, would likely prove uneconomic today because of the inventory of liquid mercury in this type of boiler. Fortunately a once-through boiler like that in SNAP-8 operates with a small inventory and would therefore offer definite economies. A substantial technology and experience, moreover, exists for once-through mercury boiling with superheat to the 650°C (1200°F) level.

Mercury is toxic, and because of its significant vapor pressure at room temperature, adequate protection must be provided for individuals exposed to it. Because of its tendency to form droplets rather than coalesce, large surface areas exposed to air are often created after a spill, thereby enhancing evaporation. Mercury can enter the food chain, a fact that has resulted in efforts by the government to strictly limit release of this metal to the environment. Because of this problem, any future mercury powerplant would have to be designed to prevent any mercury release to the environment.

Prevention of air or other containment seepage into the conversion loop is as important for the mercury cycle as it is for steam powerplants, and more so, if a refractory material, such as tantalum, is used in the boiler. Since the mercury turbine may operate at subatmospheric pressure levels at the discharge end, the performance of the shaft seal will be critical.

The impact on the environment of a mercury binary cycle coupled to a liquid-metal, fast-breeder reactor will be to reduce thermal discharges, the consumption of nuclear fuels, and the production of radioactive wastes relative to a conventional nuclear steam powerplant. The extent of these benefits will depend on the improvement in efficiency brought about by the use of the mercury binary cycle.

Potassium

The potassium topping cycle possesses some of the same problems described for the mercury system. These are concerns for materials compatibility and the ability of the turbine seal to restrict ingestion of air into the potassium loop. Problems related to the heat-transfer components and the turbine will likewise have to be studied.

The compatibility of such alloys as the low chromium - molybdenum steels, the austenitic stainless steels, and the nickel and cobalt-based alloys with potassium has not been extensively studied. Considerable work has been done, however, to determine the compatibility of many of these alloys with sodium in support of the fast breeder program (ref. 28), for example. Because of the similarity of properties of potassium and sodium, containment of potassium under the conditions required for a binary cycle is not expected to offer major difficulties if oxygen in the system can be kept low enough. The major uncertainty resides in the potential for corrosion of these alloys by the combustion products of the furnace. Coal and fuel oils contain impurities (sulfur, vanadium, alkali salts, etc.) that are detrimental to these classes of alloys. On the other hand, there are data to suggest that this attack reaches a maximum over a relatively narrow tube wall temperature band between 600° and 700° C (1100° and 1300° F) and that on either side of this band the corrosion rates are lower (ref. 16). Extra protection may therefore be required only in those exposed areas of the boiler operating within this temperature range. The combustion technique will also have a major influence on the nature and extent of corrosion. For example, fluidized bed combustion of coal generally occurs at temperatures that reduce the tendency for vaporization of the alkali impurities. In conventional coal-fired boilers, the flame temperatures are considerably higher, and the deposits on the tube surfaces frequently contain these salts.

Potassium, as mentioned previously, is readily oxidized by air. The turbine seal must effectively prevent significant amounts of air from entering the system. The buffer

seals shown in the schematic of figure 13 have been used in small potassium turbines with success. However, these will have to be scaled up and tested to insure adequacy in the large, powerplant turbines. Because corrosion of the potassium loop is increased markedly by even small amounts of oxygen, leakage of oxygen or oxygen-containing substances (such as water) into the loop must be severely restricted. Oxygen must be continually removed from the system by gettering or trapping, and oxygen levels of only a few parts per million maintained. So that these low levels of oxygen concentration might be achieved, considerable care is required in the fabrication of such components as the boiler and condenser, and a systematic plan of oxygen removal must precede the startup of the system after any repair or inspection. The cost of such care in system assembly and operation has not yet been adequately evaluated.

Rankine cycle turbines, steam included, are subject to moisture erosion of the rotor blades of the latter stages. Over the years, steam plants have evolved methods to overcome this problem. These include protective shields attached to the blade leading edges and the use of moisture extraction devices. Limited testing of potassium turbines has shown that, after 5000 hours, a microscopic amount of erosion had occurred on nickel-based blades. The blades were subjected to potassium vapor having a moisture content entering the stage of about 7 percent and to tip speeds of about 240 meters per second (800 ft/sec). Lower moisture levels gave negligible erosion. The extent to which erosion would proceed with time in a full-scale turbine is unknown. Moisture extraction devices, similar to those employed in steam turbines, have already been tested with moisture-laden potassium vapor and are considered feasible. Such devices will extend the operating life of this component.

The development of a large, low-cost potassium boiler that exhibits stable operation, relatively uniform temperature distributions, and few hot-spots will require a substantial effort. At 815°C (1500°F) the potassium boiler operates at low pressures. Liquid heads at these pressures can significantly influence the design and performance of the boiler. The liquid potassium can superheat, that is, exceed the equilibrium saturation temperature without boiling. Excessive tube-wall temperatures and boiling instabilities could result unless provisions are made to counteract this effect.

The problem of potassium leaking to the air is discussed subsequently. Another leakage problem, that of steam or water entering the potassium in the steam generator, must also be considered. This problem is analogous to the failure of a tube in the steam generator of an LMFBR plant causing the mixing of steam and sodium. The consequences of a steam-to-potassium leak have not been evaluated.

The nature of the air pollutants generated by the combustion of a fuel will not be changed through the use of a potassium topping cycle. However, because this cycle is more efficient, less fuel is required and, hence, less air pollutants per kilowatt of electricity will be produced. A reduction in waste heat can also be anticipated for the same reason.

As with mercury, consideration will have to be given to occasional leaks occurring in containment walls, such as in boiler tubes. The escaping potassium will oxidize rapidly. Consequently, a scrubbing system to prevent large releases of potassium oxide to the immediate environment will have to be incorporated within the powerplant. A large release of oxidized potassium might be harmful to life and property in the immediate vicinity of a powerplant; however, with sufficient dilution (e.g., by rain), potassium would not present a continued threat to the environment since salts of this metal are essential to life. Potassium fires are especially severe and destructive and will require some consideration in design of a powerplant; see reference 29, for example.

The effects of potassium Rankine topping cycles on the environment should be favorable. The reduction of fossil fuel consumption due to higher efficiency automatically reduces the quantity of air pollutants produced per kilowatt of electricity generated. Likewise, the waste heat discharged by the plant will be reduced.

DEVELOPMENT COSTS

Mercury Costs

No information exists on the costs of a mercury topping cycle that uses an LMFBR heat source.

Potassium Costs

Detailed information on the costs of potassium binary powerplants does not exist. However, a crude estimate of the cost of a 1000-electrical-megawatt fossil-fueled potassium-steam plant was made in reference 30. The estimated cost was \$174 million. The same reference gives the cost of a comparable steam powerplant built in the same time frame as about \$160 million. Because the topping plant was more efficient (46 percent against 40 percent), the total cost of electricity produced by this plant eventually became lower than that of the steam plant as fuel costs increased. The data of reference 30 suggest that this occurred at less than 50 cents per 10^6 Btu.

Reference 14 evaluated the costs of the ternary (gas turbine - potassium Rankine-steam Rankine) powerplant equipment. This reference concluded that the capital costs per kilowatt of output may be less than that of a conventional steam powerplant of equal capacity.

The NASA Lewis Research Center, in a joint effort with the U.S. Department of the Interior's Office of Coal Research, has initiated a small study to assess the capital costs of potassium binary plants burning coal and coal-derived fuels (ref. 31).

BENEFITS

The major advantage of the mercury and potassium binary cycles is that of increased conversion efficiency. The benefits that stem from an increase in efficiency, such as reductions in fuel consumption, waste heat release, and pollutants, will likewise accrue to powerplants utilizing the binary cycles. The disadvantages are higher capital and maintenance costs and increased complexity of the plant and its operation. The extent to which the advantages outweigh the disadvantages, if at all, is unknown and can be determined only by systematic programs involving estimation of costs, scale-up of key components and, finally, operation of pilot and demonstration powerplants. What is known, however, is that a technology base exists for each binary cycle, mercury and potassium, resulting from the space power research and development conducted over the past decade for units of very small capacity. These technology bases are believed sufficient to justify studies that consider undertaking such systematic programs.

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TABLE I. - PERFORMANCE DATA FOR MERCURY BINARY PLANTS (FROM REF. 6)

	South Meadow		GE Schenectady	Kearny	Schiller	GE Pittsfield
	Original	Replacement				
Date placed in operation	1928	1949	1933	1933	1949	1949
Type of service	Base load	Base load	Mfg. load	Base load	System load	Mfg. load
Type of fuel	Fuel oil	Fuel oil	Pulverized coal	Pulverized coal	Pulverized coal	Pulverized coal
Mercury turbine throttle conditions:				and fuel oil	and fuel oil	and fuel oil
Pressure, N/cm ² (psia)	58.6 (85)	89.6 (130)	96.5 (140)		84.1 (122)	88.2 (128)
Temperature, °C (°F)	473 (883)	508 (947)	515 (958)		503 (937)	507 (944)
Mercury turbine exhaust conditions:						
Pressure, N/cm ² (psia)	0.951 (1.38)	1.034 (1.5)	0.848 (1.23)	0.896 (1.3)	1.468 (2.13)	1.93 (2.80)
Temperature, °C (°F)	248 (478)	252 (485)	244 (471)	246 (475)	264 (508)	277 (530)
Mercury turbine flow, kg/sec (lb/hr)	136 (1.08×10 ⁶)	207 (1.64×10 ⁶)	270 (2.14×10 ⁶)	277 (2.2×10 ⁶)	^a 123 (0.98×10 ⁶)	123 (0.98×10 ⁶)
Number of mercury turbines	1	1	1	1	2	1
Number of mercury boilers	1	1	1	1	2	1
Mercury turbine-generator rating (0.8 PF), MW _e	10	^b 15	20	20	17	8.4
Steam turbine-generator rating (0.8 PF), MW	12.4 E ^c	19.1 E	--	25 E	26.4	---
Total plant output, steam and mercury, MW	22.4 E	34.1 E	47 E	45 E	43.4	21.6 E

^aEach turbine.^b1.0 PF.^cE = Equivalent power generation by associated steam-turbine limits.

TABLE II. - COMPARISON OF PROPERTIES OF RANKINE CYCLE WORKING FLUIDS

Fluid	Molecular weight	Critical temperature	Critical pressure	Latent heat	Specific volume of vapor	Thermal conductivity of liquid	Sonic velocity in vapor	Specific heat of liquid	Melting point
		$^{\circ}\text{C}$	N/cm^2	MJ/kg	m^3/kg	$\text{W/m-}^{\circ}\text{C}$	m/sec	$\text{J/kg-}^{\circ}\text{C}$	$^{\circ}\text{C}$
Water	18	374.2	2 211	^a 2.438	^a 39.52	^a 0.606	^a 428.8	^a 4187	0
Mercury	201	~1540	10 582	^b .294	^b 1.30	^b 13.3	^c 237.7	^b 138	-38.8
Potassium	39	~2175	2 675	^c 2.063	^c 16.66	^c 36.3	^c 518.1	^c 762	63.2
Cesium	132.9	~1770	1 337	^d .491	^d .55	^e 18.5	^d 297.2	^d 239	28.3
		$^{\circ}\text{F}$	psia	Btu/lb	ft^3/lb	Btu/ft-hr- $^{\circ}\text{F}$	ft/sec	Btu/lb- $^{\circ}\text{F}$	$^{\circ}\text{F}$
Water	18	705.5	3 208	^a 1048.4	^a 633.3	^a 0.35	^a 1407	^a 1.0	32
Mercury	201	~2800	~15 350	^b 126.4	^b 20.9	^b 7.7	^c 780	^b .032	-38
Potassium	39	~3950	~3 880	^c 887	^c 267	^c 21.	^c 1700	^c .182	145.8
Cesium	132.9	~3220	~1 940	^d 211.2	^d 8.8	^e 10.7	^d 975	^d .057	83

^aAt 27 $^{\circ}$ C (80 $^{\circ}$ F).

^bAt 274 $^{\circ}$ C (525 $^{\circ}$ F).

^cAt 560 $^{\circ}$ C (1040 $^{\circ}$ F).

^dAt 682 $^{\circ}$ C (1260 $^{\circ}$ F).

^eAt 28 $^{\circ}$ C (83 $^{\circ}$ F).

TABLE III. - TESTING HOURS ACCUMULATED WITH POTASSIUM AND CESIUM SYSTEMS AND COMPONENTS AT TEMPERATURES ABOVE 540° C (1000° F) (BASED ON REF. 21)

[In some columns, time shown for boiler feed pump, seal, and bearing tests were accumulated during operation of turbine. Grand total: Potassium, 800 000+ hours; cesium, 23 000+ hours.]

	Potassium							Cesium
	AiResearch	GE	JPL	NASA-Lewis	ORNL	P&W	Other ^a	
	Testing hours accumulated							
Corrosion test systems:								
Boiling	1300	25 500	-----	----	62 800	12 000	-----	3500
All-liquid	----	-----	-----	----	-----	-----	156 000	----
Component test systems, boiling	5900	19 600	-----	1000	2 800	4 900	300	2500
Simulated powerplant systems	----	-----	~1000	----	10 200	-----	-----	----
Boilers	7200	40 100	1000	1000	75 800	16 900	300	6000
Turbines	3050	10 100	-----	----	5 000	-----	100	----
Boiler feed pumps:								
Electromagnetic	7200	34 600	3600	1000	26 900	4 900	3 300	5600
Turbine driven	----	-----	-----	----	5 000	-----	-----	----
Other pumps	5900	18 600	3600	1600	6 100	1 300	57 600	----
Condensers	7200	40 100	~1000	1600	75 800	16 900	300	5600
Seals	3050	10 100	-----	----	-----	-----	-----	----
Bearing tests	3000	-----	-----	----	4 500	-----	1 600	----

^aIncludes testing hours of Aerojet Nucleonics, Allison, Rocketdyne, United Nuclear.

^bIncludes testing hours of Brookhaven, Aerojet Nucleonics, Westinghouse Astronuclear.

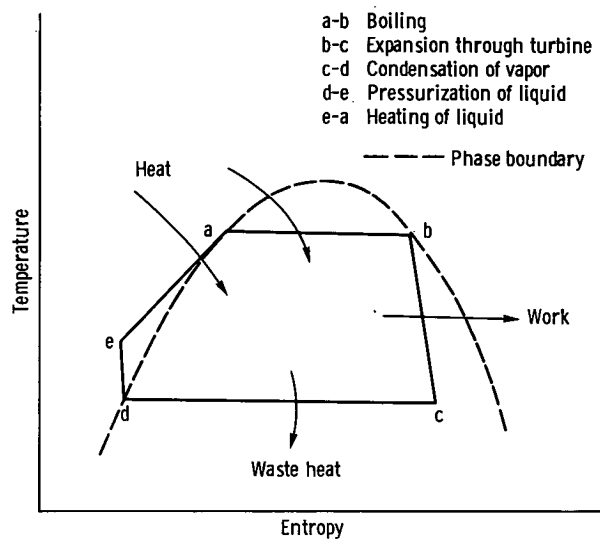


Figure 1. - Simplified steam Rankine cycle.

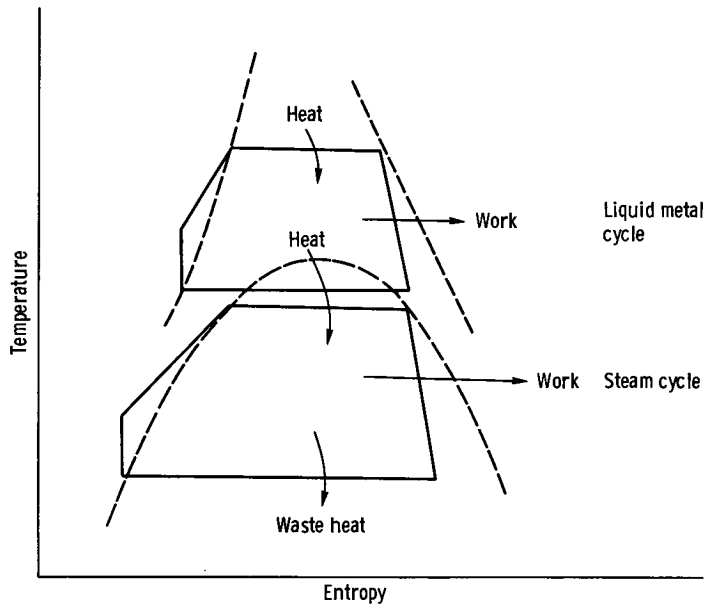


Figure 2. - Simplified liquid metal binary Rankine cycle.

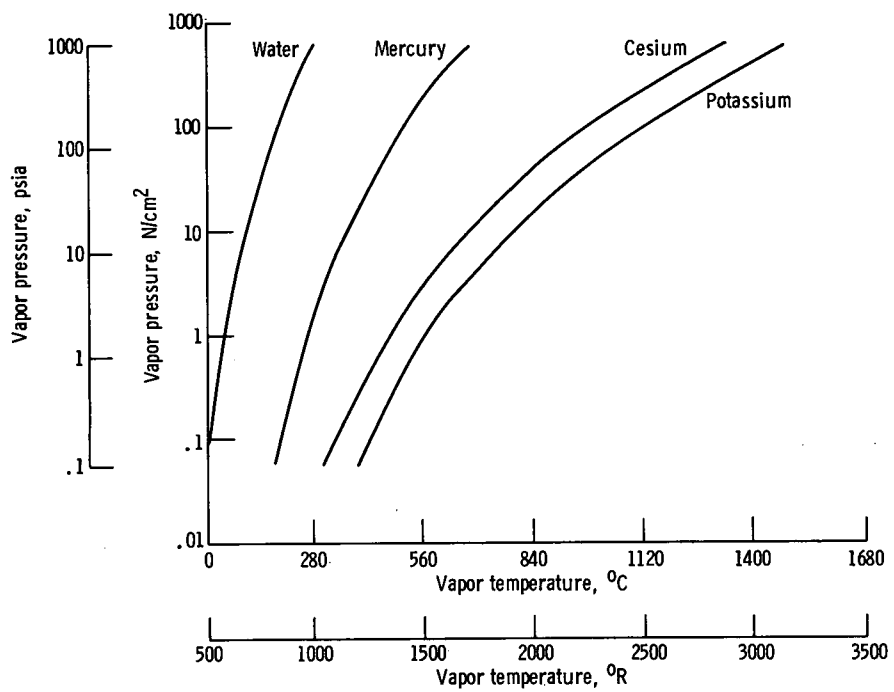


Figure 3. - Vapor pressure as function of temperature for Rankine cycle working fluids.

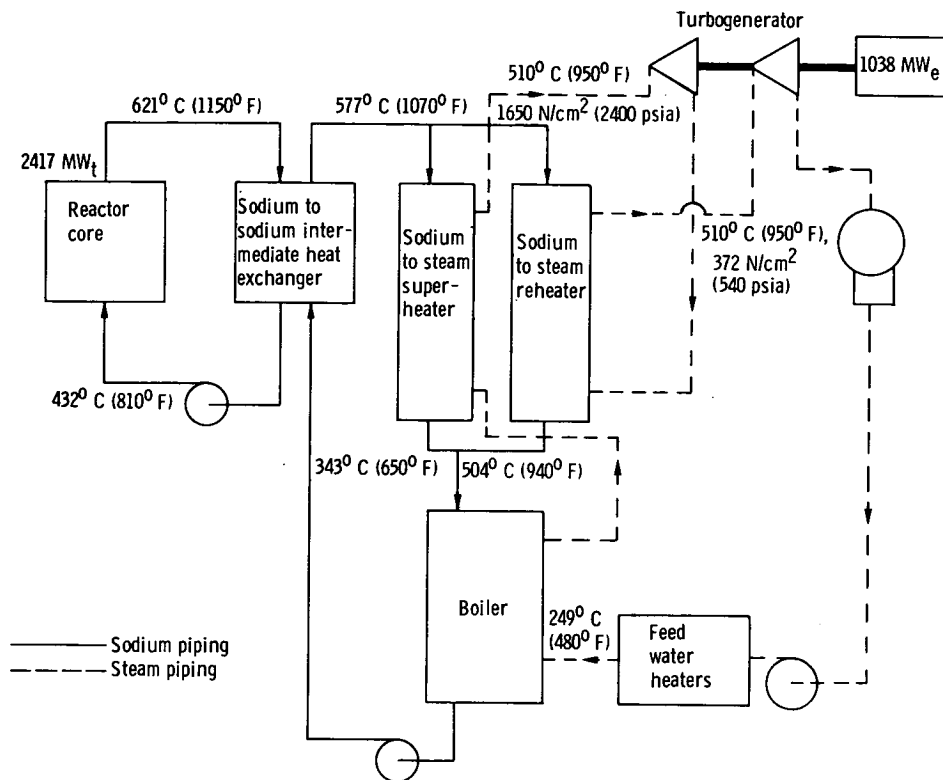


Figure 4. - Schematic of steam system for liquid-metal, fast-breeder reactor (efficiency, 41.6 percent).

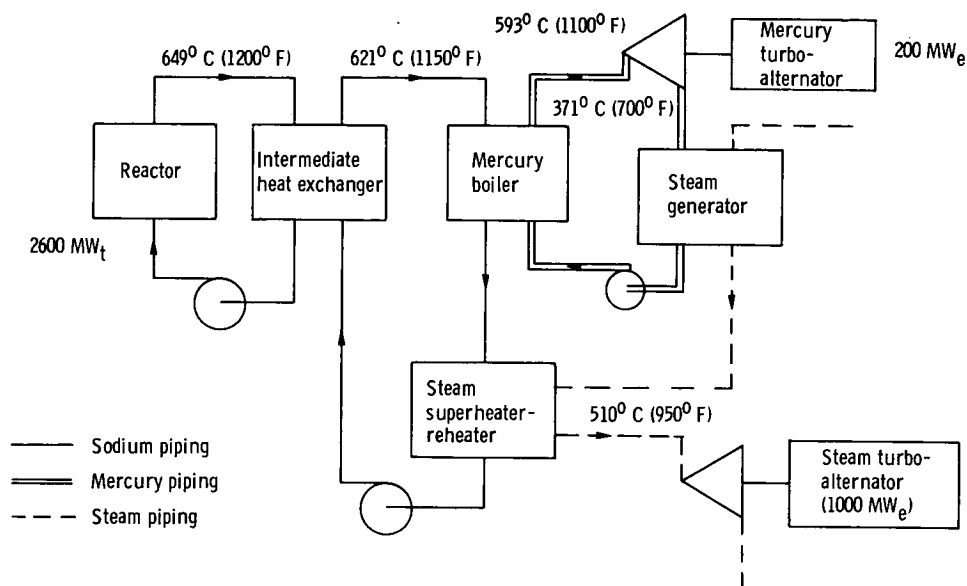


Figure 5. - Liquid-metal, fast-breeder reactor with mercury topping cycle (efficiency, 46 percent).

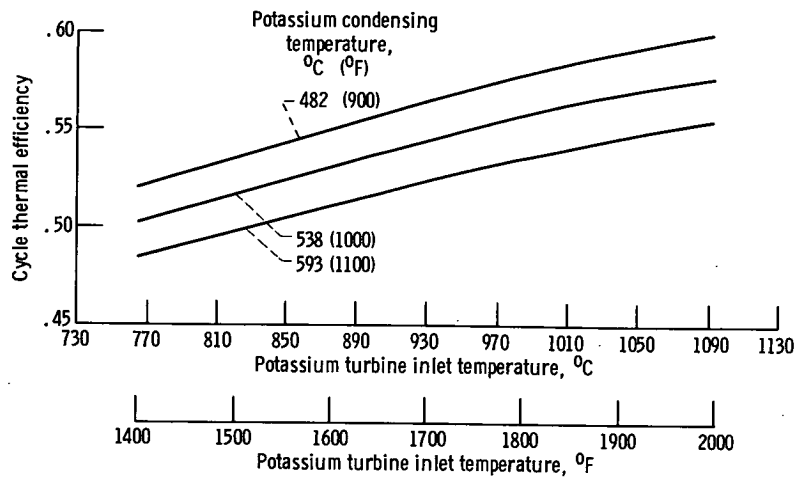


Figure 6. - Potassium binary cycle efficiencies. (Assumes boiler efficiency of 0.9.)

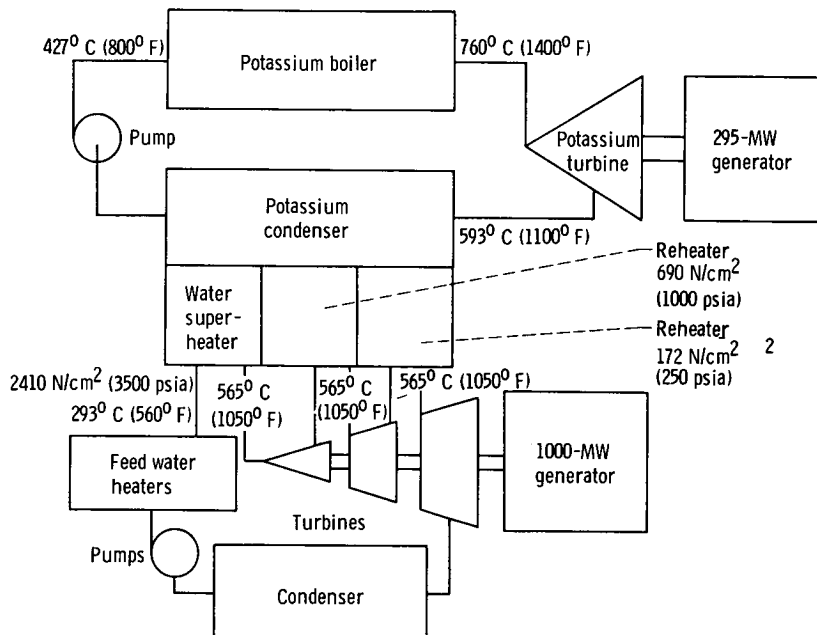


Figure 7. - Schematic of combustion-heated potassium binary cycle (ref. 16).

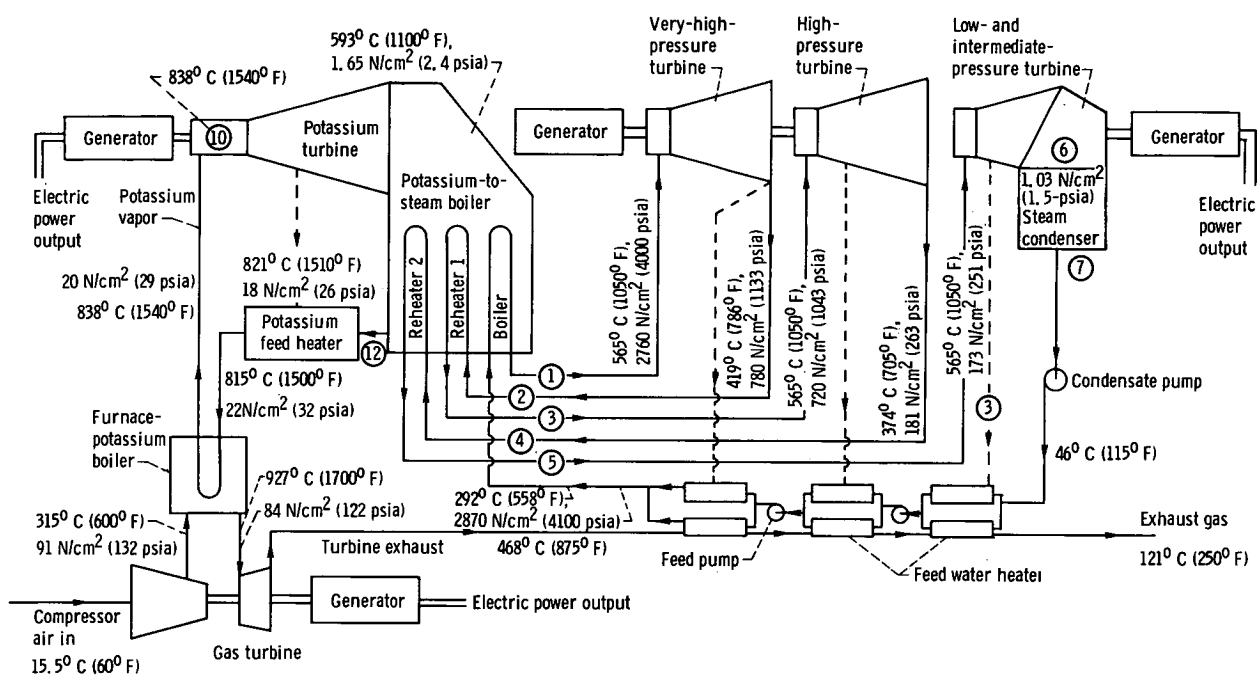


Figure 8. - Schematic of gas-turbine - potassium Rankine - steam Rankine ternary cycle (ref. 14).

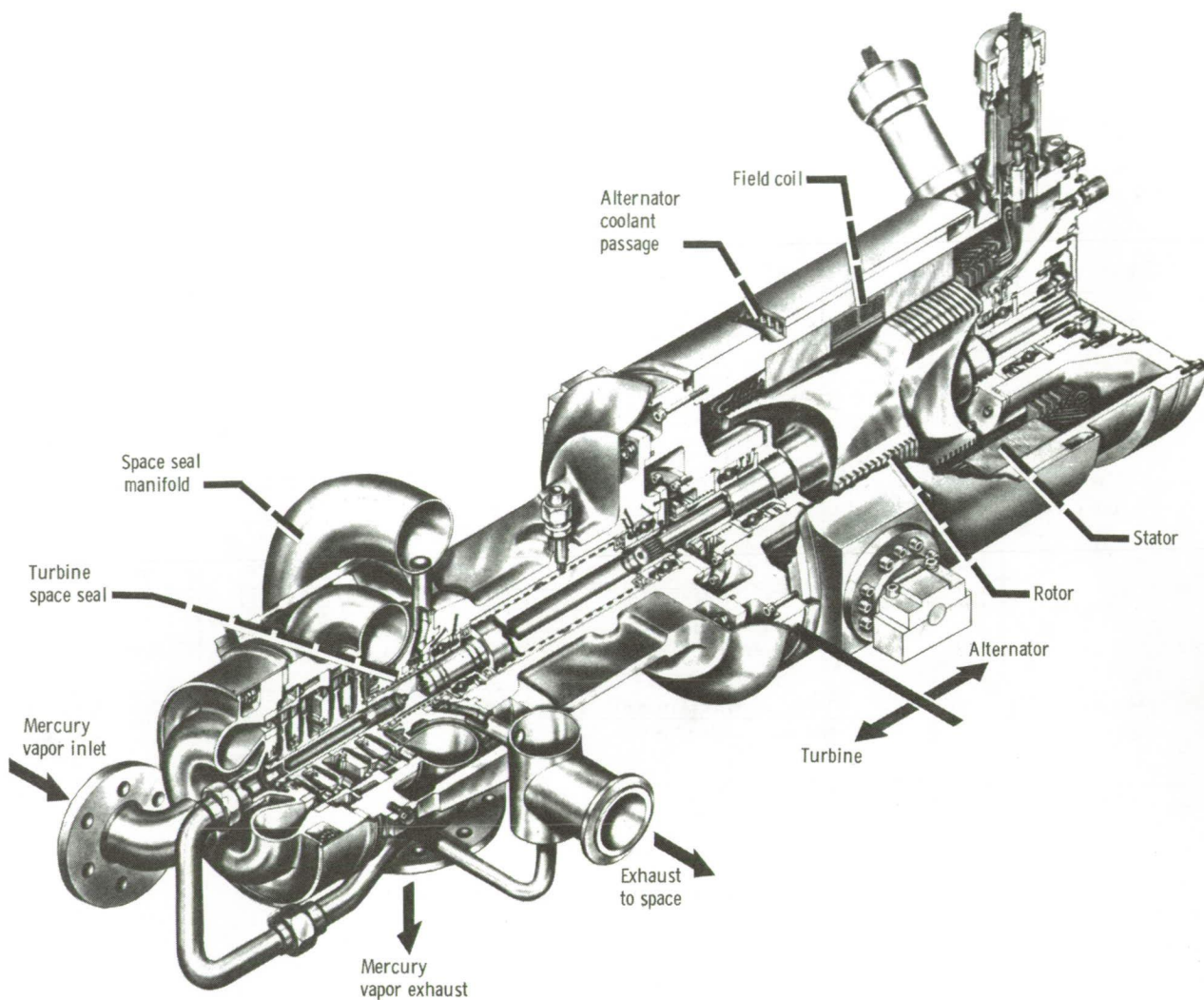


Figure 9. - SNAP-8 mercury turbine alternator assembly.

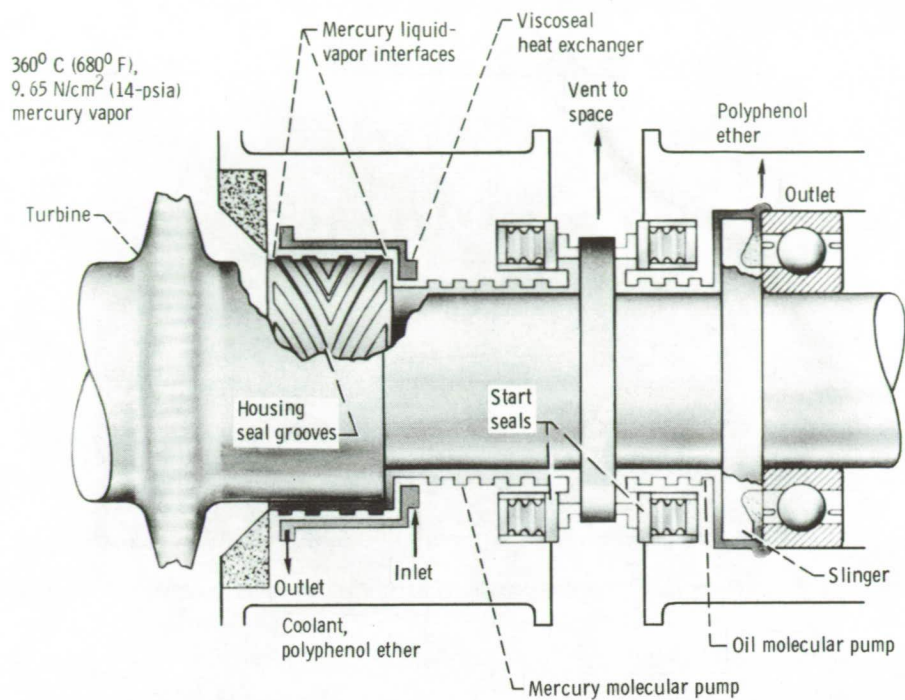


Figure 10. - SNAP-8 mercury turbine-alternator assembly seal.

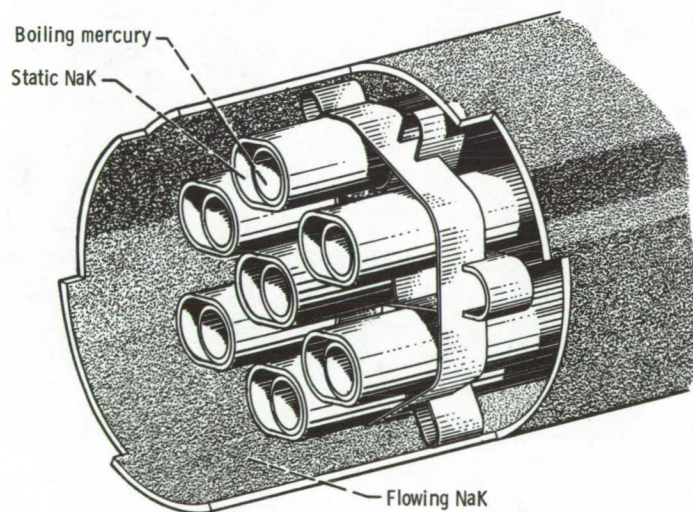


Figure 11. - SNAP-8 boiler tubes.

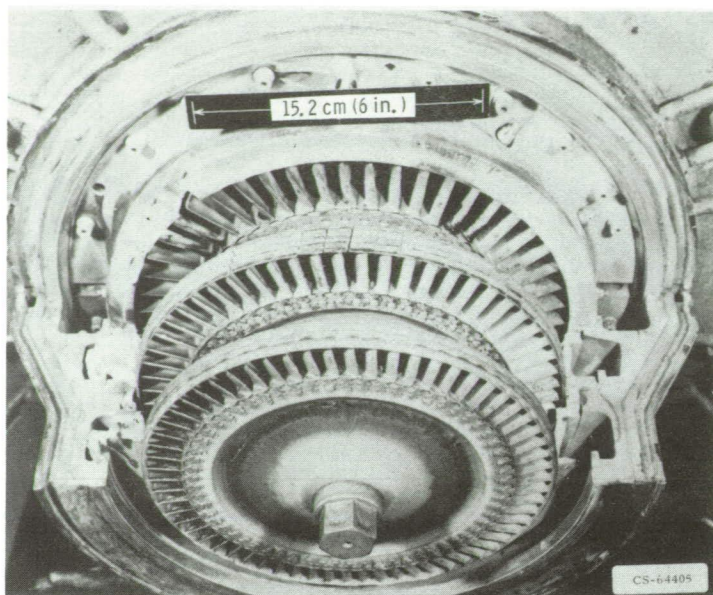


Figure 12. - Three-stage potassium turbine after 5000 hours operation.

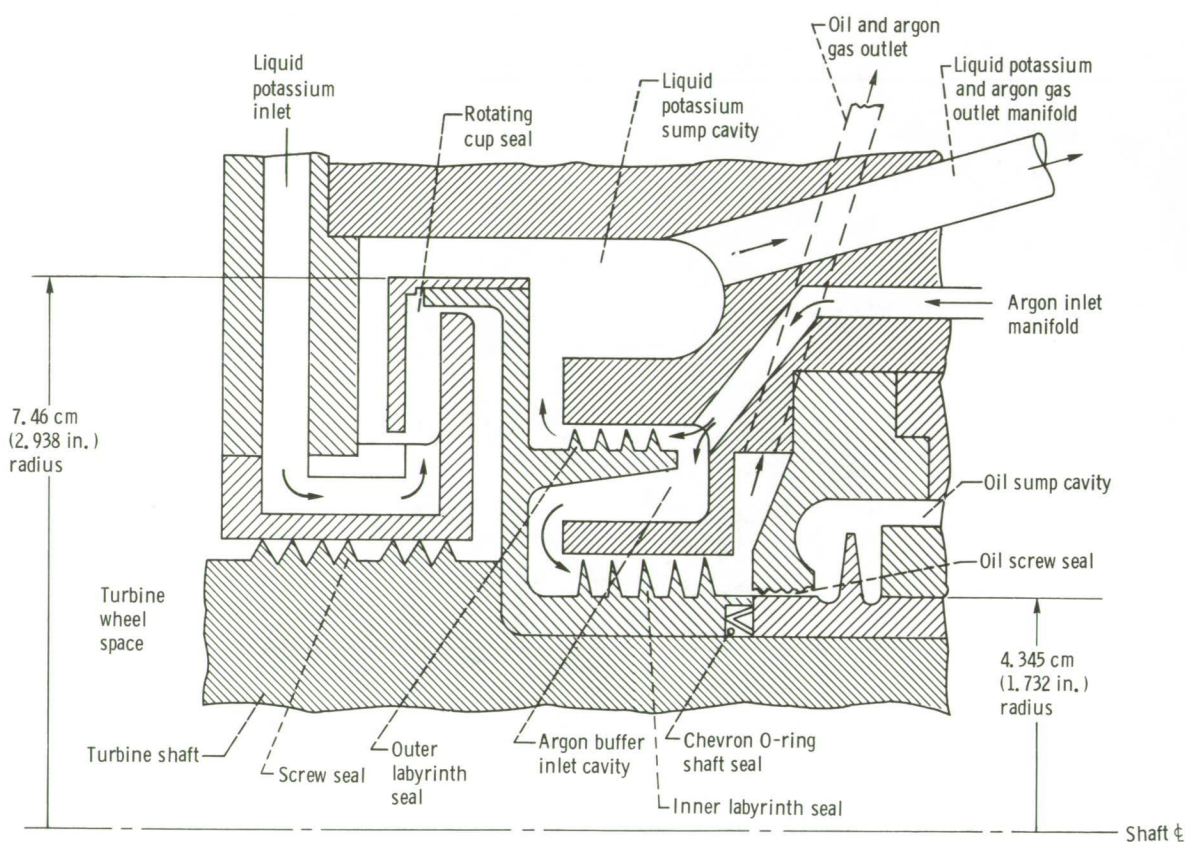


Figure 13. - Section view of two- and three-stage potassium vapor turbine hydrodynamic seal assembly (19 250 rpm).



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